Arabian Journal of Chemistry (2014) xxx, xxx–xxx

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Chemically modified multiwalled carbon nanotube carbon paste electrode for copper determination

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Received 22 October 2012; accepted 16 November 2013

KEYWORDS

Carbon paste electrode,
Chemically modified multiwalled carbon nanotube;
Copper ion;
Ag nano particle;
Potentiometric sensors

Abstract A new Cu^{2+} carbon paste electrode based on incorporation of new CPE via chemically modified multiwalled carbon nanotube (CMMWCNT) on the graphite matrices has been constructed. The surface of MWCNT was modified by performing a coupled reaction between trimethoxysilylpropylethilendiamine (TMSPEDA) and 2-hydroxybenzaldehyde (2-HBA). This new material was characterized with different techniques such as FT-IR, SEM and BET analysis. The influence of variables including sodium tetraphenylborate (NaTPB), graphite powder, Nujol, amount of MWCNT–SPAEIMP and Ag nano particles loaded on AC on the electrode response was studied and optimized. At optimum values of variables set as carbon powder, carrier, NaTPB and Nujol, the response of Cu^{2+} selective electrodes in the absence and presence of Ag-NP-AC was linear in a concentration range of 5.0×10^{-6}–1.0×10^{-1} and 5.0×10^{-7}–1.0×10^{-1} mol L^{-1} with slope 29.93 and 29.11 mV and with detection limit of 3.2×10^{-6} and 2.5×10^{-7}. The good performance of electrode viz. reasonable wide pH range (2.0–5.5), fast response time (< 15 s) and adequate life time (2 months) in addition to low RSD (< 4%) shows the utility of the proposed electrodes for Cu^{2+} ion content quantification in various situations. The moderate selectivity coefficient evaluated by the separation solution method (SSM) and fixed interference method (FIM) indicates efficiently the discriminating ability of proposed electrode for copper ion evaluation.

1. Introduction

The research on fabrication of new ion sensors has caused a fundamental development in potentiometry over the past few decades (Umezawa, 1990). Ion selective electrodes (ISEs) are well known and efficient tools for accurate and repeatable determination of various target molecules or ions in biological and industrial analysis. In view of distinct advantage of ISEs huge amount of efforts have been devoted to make selective sensors for different ions (Daunert et al., 1991).

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2013.11.029

In addition to conventionally constructed electrode, the carbon paste type electrode has become attracted and wide application for potentiometric determination of target species. The development and application of potentiometric sensors are extensively concern to the usage of selective recognition elements (ionophore). Among various classification of mechanism of ISEs response, the carrier-based ion-selective electrode (ISEs) on the basis of chemical recognition principles has the best characteristic performances (Gupta et al., 2009). One of the most prominent problems in ISEs is the leaching of ionophore to the bulk sample solution that strongly is forbidden by application of chemically modified ionophore. Carbon paste electrodes (chemically modified carbon paste electrodes (CMCPEs)), are fabricated in a simple way. CMCPEs based on modification of MWCNT surface due to enhancement in charge transfer and the number of surface reactive atom and surface area lead to improvement in electrochemical response. In such electrodes, a stable electrochemical response can be obtained following renew of electrode surface by removing an outer layer of the paste and re-smoothing the electrode surface.

Copper contents have great importance and diverse role in various biological, human life and industrial activities. Long-term exposure of human to copper ion causes irritation of the nose, mouth and eyes in addition to headache problems (Jain et al., 1995a,b; Rosatzin et al., 1993; Shamsipur et al., 1999). Because of this widespread appearance and application and high amount of tolerable copper content (2 mg L^{-1}), its determination has great importance. Its excessive intake manifests in certain human diseases such as Menke's syndrome and Wilson's disease. Therefore, Cu^{2+} ion determination is important in term of its utility and toxicity. Different analytical methods are being used for the determination of Cu^{2+} ion (Narin et al., 2001; Ozdes et al., 2012; Saracoglu et al., 2002, 2003; Soylak and Kariper, 2010). Application of ion-selective electrodes (ISEs) makes possible accurate, rapid, non-destructive and low cost, fast response and convenient analysis with easy handling and any sample pretreatment (Bakker and Meyerhoff, 2000; Biesaga et al., 2000; Gouterman, 1978; Ortiz de Montellano, 2010; Ochsenbein et al., 1994; Shokrollahi et al., 2009).

In recent years, great attention has been devoted to the application of nano-structure materials, especially carbon nanotubes (CNTs). In particular, there have been an increasing number of applications of CNTs in several chemical analysis fields (Duran et al., 2009; Soylak, 2007; Tuzen et al., 2008a,b). The combination of specific metal–ligand interaction and addition of carbon nanotubes (CNTs) is the most important recognition mechanism (Ajayan, 1999; Bianco et al., 2005a,b; Ghaedi et al., 2005; Klumpp et al., 2006; Li et al., 2008; Rezaei and Damiri, 2008; Siswana et al., 2008) facilitating the electron transfer between the electro-active species and the electrodes.

Generally, chemically modified electrodes (CMEs) (Akhond et al., 2005; Amini et al., 2003; Ghaedi et al., 2005, 2010; Giasmera et al., 2006; Shokrollahi et al., 2009) are formed by covalent binding of mono or multi layers of molecules on the electrode surface. Low selectivity and efficiency of untreated or oxidized-multiwalled carbon nanotubes (MWCNT) may be a concern to the presence of $–NH_2$ and –COOH (Ganjali et al., 2009; Wang et al., 2008). The change in the nature of surface by suitable materials generally improves selectivity and sensitivity of the determinations (Sherigara et al., 2004; Steinle et al., 2002; Zhao et al., 2002). The most selective interaction trend for preparation of copper selective electrodes is based on application of chemical recognition elements (organic or inorganic hydrophobic chelating agent) with selective tendency for binding of Cu^{2+} ion (Ochsenbein et al., 1994; Biesaga et al., 2000; Shokrollahi et al., 2009; Bakker and Meyerhoff, 2000; Akhond et al., 2005; Amini et al., 2003; goyal et al., 2007; Amini et al., 2003; Gismera et al., 2003; Hassan et al., 2005; Fakhari et al., 2005; Singh et al., 2006). Most of the previously reported electrodes in view of their advantage suffer from limitations such as low linear range, high detection limit and response time (Table 1). In our sense, these limitations can be overcome by simultaneous incorporation of nanoparticles and chemical immobilization of carbon surface.

The introduction of nanostructured material enables the development of new potentiometric sensors via replacing the polymeric membrane with the transducers. The functionalization of carbon nanotubes makes possible the direct linkage of the receptor molecules as an alternative pathway instead of entrapping which improves the electrode performances. These types of sensors are very different from ISEs in terms of: (1) the receptor is immobilized onto the walls of carbon nanotubes instead of being entrapped in a polymeric membrane; (2) the receptor is in direct contact with the target, and the recognition event is based on an affinity process; (3) the targets are not necessarily small ions, but instead can be large multiunit species such as proteins or complex systems such as microorganisms; (4) the sensing mechanism is based on a superficial phenomenon, very different from the well-established phase-boundary potential model in ISEs; (5) the sensing mechanism is based on the potential generated by the different charged species in the chemical environment of the nanotubes, which in turn means that the calibration curves do not follow the classical Nernstian model; (6) the sensitivity of the new sensors is very low compared with that of ISEs, but it is high enough to enable the detection of the target (Ghaedi et al., 2011).

In progress of our other attempts, new copper selective electrodes based on the synthesis of CMMWCNT was applied for design of Cu^{2+} ion carbon paste electrodes. In this paper, MWCNT-SPAEIMP (product of reaction between trimethoxysilylpropylethilendiamine (TMSPEDA) and 2-hydroxybenzaldehyde (2-HBA)) was chemically bonded to MWCNTs to produce a new material (MWCNT-SPAEIMP) for preparation of new Cu^{2+} ion selective electrode.

2. Experimental detail

2.1. Apparatus, reagents and materials

Analytical-reagent grade ethanol and methanol were supplied from Fluka (Buchs, Switzerland). All the potential and pH measurements were carried out with a pH/Ion meters model 780 (Metrohm Co., Herisau, Switzerland). All chemicals used were of analytical reagent grade and doubly distilled water was used throughout. Graphite powder and high purity Nujol oil from Fluka (Buchs, Switzerland) were used for the preparation of the modified carbon paste electrode. The stock solution of 0.5 M Cu^{2+} ion was prepared by dissolving appropriate amount of nitrate salt form Merck (Darmstadt, Germany) in 100 mL doubly distilled water. MWCNT with the highest purity available purchased from Merck (Darmstadt, Germany) was used. The ionophore MWCNT-SPIMP (Fig. 1), was

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Table 1 General Performance characteristics of some copper ion sensors based on various organic ionophores.

Ionophore	L.R.[a]	Slope[b],	D. L. (μM)	I[c]	pH	R.T[d]	Refs.
Thiacrown ethers	10–0.1	22.3	0.14	Pb^{2+}	–	–	Gupta et al. (2000)
ACCP	10–0.2	29.4	8.0	–	–	–	Park et al. (2001)
–	7.94–0.1	29.9 ± 0.2	–	Na^{+}, Co^{2+}	2.1_6.3	11	Abu-Shawish et al. (2008)
–	10–0.1	Nernstian	–	–	1.9–5.2	<30	Zhang et al. (2009)
Porphyrin	4.4–0.1	29.3	0.28	Ni^{2+}	2.8–7.9	~8	Jain et al. (1995)
TDS	–	31	0.4	K^{+}, Zn^{2+}, Pb^{2+}	–	–	Gholivand et al. (2007)
NDHA	0.3–0.01	30.0 ± 0.5	0.25	–	3.0–7.4	<10	Li et al. (2009)
SFP	0.23–0.001	29.4 ± 0.5	0.027	–	2.3–5.4	8	Maity and Chattopadhyay (2006)
Dithiocarbamate	1.0–0.1	28–29	0.4	–	–	–	Kkumar and Pallavi (2007)
TDTSA	0.025–0.0006	68.7	0.013–0.5	Pb^{2+}, Mg^{2+}, Cd^{2+}, Ca^{2+}, Al^{3+},	–	–	Bakker and Meyerhoff (2000)
PTD	0.97–0.076	30 ± 2	0.77	NR	–	–	Ghaedi et al., 2012
MD	32–0.1	30	12	Sr^{2+}, Cs^{+}, K^{+},Na^{+}, Sr^{2+}	–	–	Sadeghi et al. (2003)
–	8–0.1	29.5	1.0	Pb^{2+}, Al^{3+}	–	–	Shokrollahi et al. (2009)
–	1–0.01	30.0	>0.1	–	–	–	Gupta et al. (2005)
Calixazacrown ethers	0.031–0.0031	27.2	10.0	Rb^{+}	–	–	Gupta et al. (2002)
CTP	1–0.01	30.3	0.75	Zn^{2+}, Pb^{2+}	4.5–7	15 and 20	goyal et al. (2007)
ACA	0.22–0.01	29.2 ± 0.2	0.11	Ag^{+}	4.0–9	15	Shokrollahi et al. (2009)
BHAB	0.05–0.01	29.6 ± 0.2	0.04	–	2.8–5.8	15	Lee et al. (2008)
–	5.0–0.1	29.88	2.34	–	2.8–7.5	10	Zamborini et al. (2001)
BAPE	10–0.1	30.0	0.5	–	3.3–7.0	10	Kamata et al. (1989)

Abbreviations: ACCP, Aza-thio ether crowns containing 1,10 phenanthroline; BHAB, Bis(2-hydroxyacetophenone)butane-2,3-dihydrazone; HIPM, Hydrotris(3isopropylpyrazolyl)methan; BAPE, bis(acetylacetone)propylenediimine; PPTD, 3-(2-pyridinyl)-2H-pyrido[1,2,-a]-1,3,5-triazine-2,4(3H)-dithione; EBCC, Ethambutol–copper (II) complex; TDS, Thiuram disulphides; NDHA, N,N′-(2,2-dimethylpropane-1,3-diyl)-bis(dihydroxyacetophenone); SFP, salicylidine-functionalized polysiloxane; TDTSA, Thio and dithiosalicylic acids; PTD, Pyrimidine thione derivatives; MD, Macrocyclic diamides; CTP, cyclic tetrapeptide; ACA, acetoacetanilide.

[a] Linear range (μM-M).

[b] (mV per decade concentration).

[c] Interference.

[d] Response time (s).

synthesized in our laboratory. Typical procedure for the synthesis of ionophore is explained in Section 2.2.

2.2. Synthesis of chemically modified MWCNT with 2-((3silylpropylaminoethylimino) methyl) phenol (MWCNT-SPAEIMP)

The CMMWCNT was prepared according to our previous reports in three stages including activation of MWCNT, supporting of organic spacer (trimethoxysilylpropylethilendiamine (TMSPEDA)) and finally generation of Schiff base chelate on it. This work was performed by treatment of 1.0 g of MWCNT with 250 mL of 4 M nitric acid under severe stirring for 36 h at room temperature. Then the mixture was filtered and washed several times with double distilled water and dried for 1 day at room temperature. After this, the activated MWCNT were treated with 1.8 mL of TMSPEDA in dichloromethane under reflux for 24 h. The Schiff base chelate generation on the surface was carried out by addition of 2.2272 g of 2-hydroxybenzaldehyde (2-HBA) to suspension of previously obtained solid in methanol (25 mL) and then refluxed the reaction mixture for 24 h. In final, *CMMWCNT* greenish black solid entitled as MWCNT-SPAEIMP was filtered and washed three times with methanol and dried at room temperature. The schematic diagram of MWCNT-SPAEIMP preparation is presented in Fig. 1.

2.3. Synthesis of Ag nanoparticles

The Ag nanoparticles (Ag NPs) were synthesized in a one-step reduction process in an aqueous solution. All reactions were carried out in oxygen free water under nitrogen. Following addition of 400 μL of 0.1 M $AgNO_3$ into 100 mL of 0.15 w/w% of starch solution, the mixture was stirred vigorously for 1 h at pH of 8.0. In these conditions, the initial reaction mixture was colorless and the growth of the Ag NPs was monitored at different intervals using an UV–Visible absorption spectroscopy. Formation of turned light yellows following about 1 h shows production of the Ag NPs and after keeping at 50 °C for 24 h the reaction color became yellow. In the next step, 10 g AC was added to the mixture in a 250 mL flask and stirred for up to 12 h. This treatment led to deposition of the Ag NPs on the activated carbon (Ag NPs-AC). The Ag NPs-AC were then filtered and extensively washed with double distilled water. A mortar was used to homogeneously ground the Ag NPs-AC powders. The Ag NPs-AC was stored in air at room temperature and was found to have a shelf life of at least 1 year.

2.4. Electrode preparation and potential measurements

Carbon paste was prepared by hand mixing of 50 mg of reagent-grade graphite powder and 100 mg CMMWCNT, 5 ml THF and 18 mg of Nujol oil with a mortar and pestle. Modified carbon nanotube paste electrodes were prepared by hand mixing different amounts of Ag nano particle with 50 mg of reagent-grade graphite powder and 36 mg of Nujol oil with 100 mg CMMWCNT and additive (NaTPB) dissolved into THF to get different compositions. The solvent evaporated by stirring. Both unmodified and modified pastes were

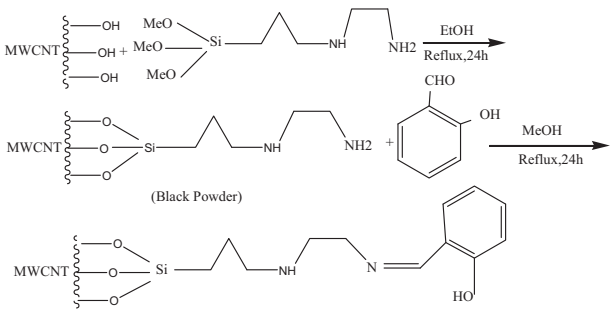

Figure 1 Schematic diagram of synthesis of chemically modified MWCNT.

packed into the end of polyethylene tube (*ca.* 3.4 mm *i.d.* and 2.0 cm long). Electrical contact was made by inserting a copper wire into the polyethylene tube at the back of the mixture. When necessary, a new surface was obtained by pushing an excess of paste out of the tube and polishing it on a weighing paper.

2.5. Measurements of electromotive force (emf)

All measurements of emf were made at 25 °C by a Metrohm pH/Ion meter, model 780 (Metrohm Co., Herisau, Switzerland) with a double junction Ag/AgCl, and KCl (saturated) electrode as reference electrode in the cell assembly as follows:

Ag/AgCl||Cu^{2+} ion solution |CPE|Cu wire. Absorbance measurements were carried out with a Jasco model V-570 spectrophotometer (Jasco Co., Hachioji, Tokiyo, Japan) and atomic absorption measurements were carried out by the use of a Varian Spectra AA model 220 (Varian Co., Walnut Creek, CA). 1H NMR, FT-IR and GC–Mass spectroscopies were, respectively carried out with Bruker 250 MHz (Bruker Co., Ettlingen, Germany), Shimadzu FTIR-8300 and Shimadzu GCMS-QP1000EX spectrophotometers (Shimadzu Co., Tokiyo, Japan).

2.6. Pretreatment of real sample

Homogenized real sample 20 g weighted accurately in a 100 mL beaker was digested in the presence of an oxidizing agent with addition of 10 mL concentrated HNO_3, 3 mL H_2O_2 30 (w/w%) and 5 mL $HClO_4$ 70 (w/w%) following heating for 1 h. The content of beaker was filtered through a Whatman No. 40 filter paper and again 5 ml concentrated HNO_3, 3 ml H_2O_2 30 (w/w%) were added and heated for 1 h, then diluted to 500 mL with distilled water. Then its pH was adjusted and the above procedure for determination of copper content was applied. The copper content was evaluated by the standard addition method.

3. Result and discussion

The synthesized CMMWCNT was characterized by FT-IR, SEM and BET as show in Fig. 2a–c, Figs. 3 and 4. The FT-IR-spectroscopy, SEM and BET data are used to prove chemical modification of the MWCNTs' surface. The IR spectrum of activated MWCNTs(Fig. 2a) shows absorption frequencies at 3400–3600 (bw), 1627(s), 1155(s), 673(s), and 592(s) cm^{-1} maybe assigned to vibrations of OH, C═O, C–O, and C═C groups. After supporting the TMSPEDA on activated MWCNT, its IR spectrum (Fig. 2b) exhibited some new absorption frequencies such as 2911(w), 2890(w), 1635(w), 910(w), 1553(w), 1031(s), and 1098(s) assignable to stretching and/or bending of C–H, N–H and C–N in new added organic moiety to surface confirming its binding. Finally, the Schiff base modification of surface to obtain MWCNT-SPAEIMP is proved by the appearance of characteristic absorption frequencies (Fig. 2c) such as 3408(m), 3073(w), 2857(w), 1622(s), 1582(s), 1528(m), 1299(m), 1111(s), and 964(m) that may be attributed to O–H, aromatic C–H, iminic C–H, iminic, C═N, benzene ring C═C, C–N, C–O vibrations and out of plane bending of O–H respectively. The response feature of the copper CPE such as response time, life time, selectivity

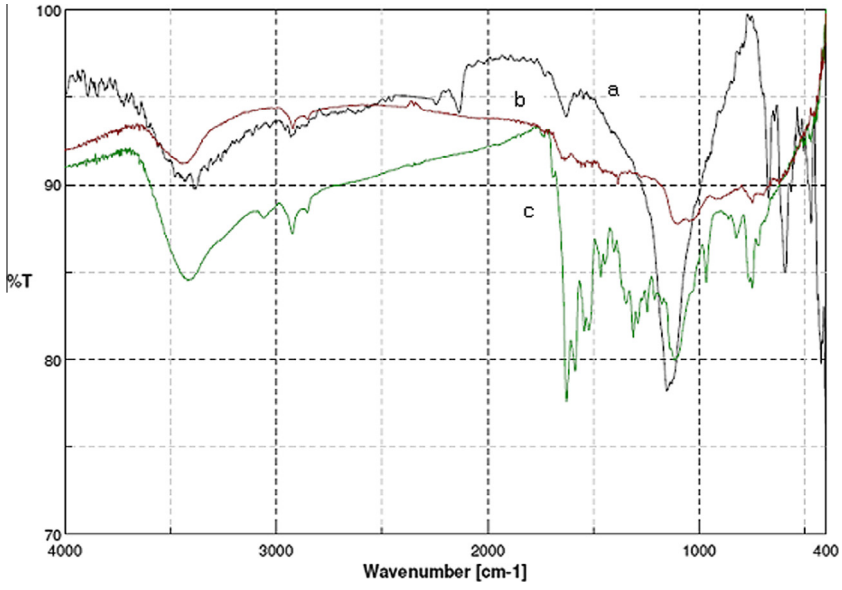

Figure 2 FT-IR of activated MWNCT (a), MWCNT- TMSPEDA (b) and MWCNT-SPEDIMP as CMMWCNT (c).

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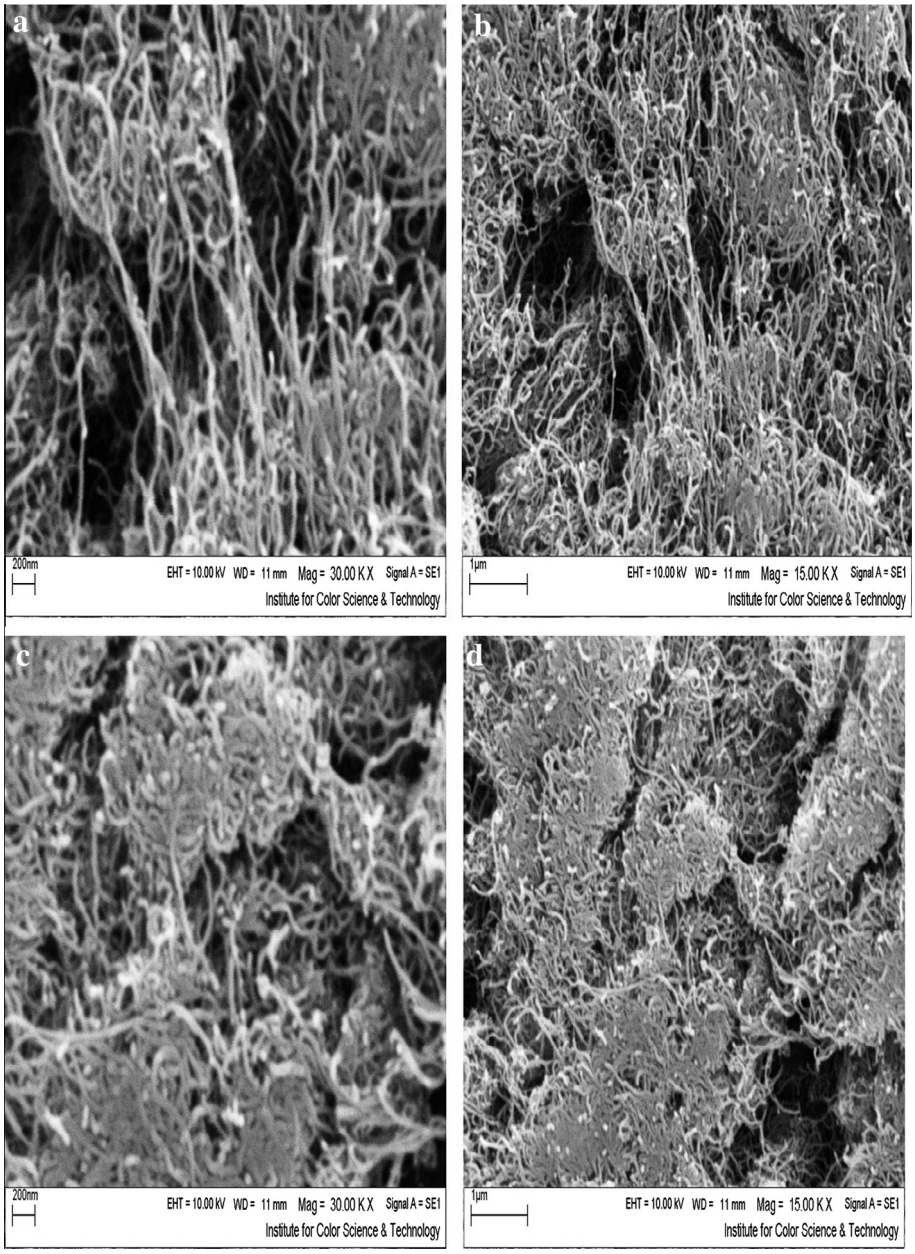

Figure 3 SEM of chemically modified MWCNT.

and chemical stability depends on the ratio of electro-active phase and the binder material (Zhang et al., 2009). Understanding the chemical and physical processes including the ion fluxes in the sensing layer (contains the ionophore) led to very low limits of detection and increases selectivity. Generally, omitting the inner water solution improved the performance of the electrodes (Bobacka et al., 2008; Fibbioli et al., 2000). To investigate the influence of amount of carbon paste ingredients on the electrode response, response properties of similar electrodes incorporating various amounts of chemically modified MWCNT have been recorded and respective results show that increasing amount of chemically modified MWCNT to 25 mg led to achieve the Nernstian potentiometric response and further addition causes decrease in response properties such as linear range and slope (Table 1). These behaviors probably can be related to change in stoichiometry of complexes of metal ions with carrier or surface saturation and in-homogeneity of carbon paste matrices. Generally, addition of lipophilic additive in ion selective electrodes by simultaneously reducing ohmic resistance and increasing the rate and kinetic of mass transfer enhances the response behavior and selectivity of the membrane electrodes. On the other hand, the perm-selectivity optimization of the membrane sensor is known to be highly dependent on the incorporation of the additional components. It was found by addition of various increment of NaTPB until 10 mg the response properties significantly improved and at higher value due to probable competition of additive with ionophore, linear range and detection limit significantly diminished. Also at lower value, because of low perm-selectivity and higher counter ion fluxes to carbon paste, linear range

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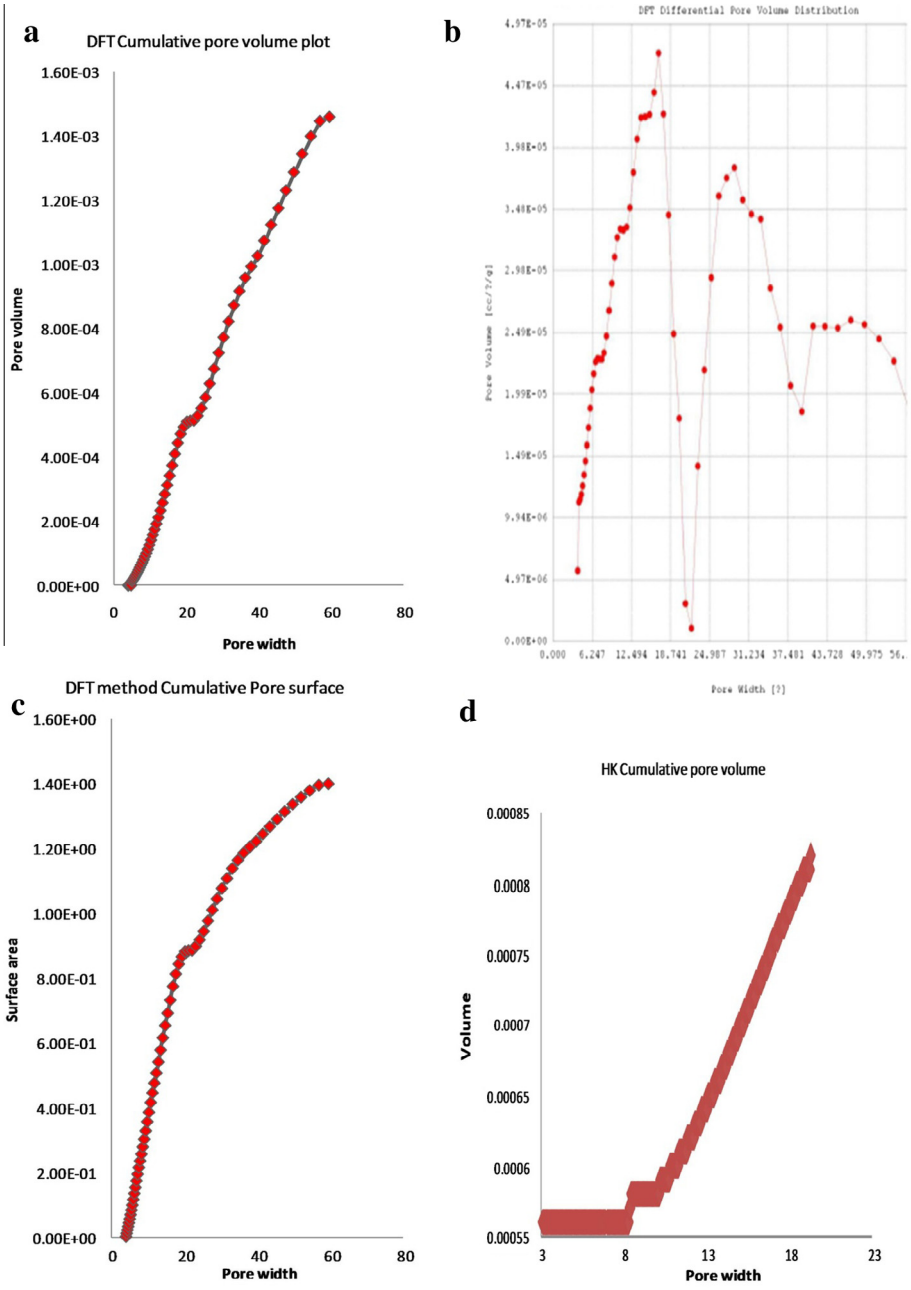

Figure 4 BET of chemically modified MWCNT.

and slope diminished. In order to improve the response properties of proposed electrode Ag nanoparticle loaded on AC and oxidized MWCNT were impregnated to carbon paste matrices and their response properties in the concentration range of 1×10^{-9}–1×10^{-1} M were investigated and results are present in Table 2. As it can be seen, addition of Ag-NP-AC to carbon paste matrices (*t*-test) significantly improves the linear range and detection limit of electrode response that may be attributed to an increase in the conductivity of the sensor and the transduction of the chemical signal to electrical. This phenomenon can be explained by the fact that nanomaterials display new properties not shown in the bulk material. Their extremely high surface-to-volume ratio and surface atom promote a greater interaction with targets as part of the recognition layer. Another probable mechanism is high charge transfer and the extraordinary electrical capacities generated at the interfaces of some nano-structured materials. This behavior has a great role and significant when nanomaterials are the transducing components of potentiometric sensors.

The high stability of the recorded potential of an electrode based on nanostructured materials is a concern to the high double layer capacitance attained from their very large surface to volume ratio. These potentiometric sensors have extremely low limits of detection and significant selectivity coefficients in addition to simplicity, low cost and labelless detection.

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Table 2 Response performance of the copper carbon paste electrodes at different compositions based on CMMWCNT.

N	Carbon powder (mg)	Carrier (mg)	NaTPB (mg)	Nujol (mg)	Ag-NP(mg)	L. R. (μM-M)	Slope (mV/decade)
1	50	10	2.0	18	0	0.1–0.01	3.09
2	50	30	2.0	18	0	1.0–0.01	6.09
3	50	60	3.0	18	0	50.0–0.01	18.33
4	50	80	6.0	18	0	0.5–0.01	14.54
5	50	100	2.0	18	0	1.0–0.05	17.24
6	50	120	6.0	18	0	50.0–0.01	46.45
7	50	100	4.0	18	0	5.0–0. 1	29.27
8	50	100	6.0	18	0	1.0–0.1	30.84
9	50	100	8.0	18	0	1.0–0.1	38.14
10	50	100	6.0	36	0	1.0–0.1	29.93
11	50	100	0.0	36	0	5.0–0.1	13.08
12	50	100	6.0	36	3.0	0.5–0.005	24.27
13	50	100	6.0	36	5.0	0.1–0.1	29.11
14	50	100	6.0	36	7.0	5.0–0.01	29.98
15	50	100	6.0	36	8.0	10.0–0.1	29.21
16	50	100	6.0	36	10	0.5–0.01	32.01

The functionalization of nanostructured materials via different sensing layers through various pathways such as covalent and non-covalent bonding and entrapment or encapsulation of the receptors in the nanoparticles (Frasco and Chaniotakis, 2010; Giljohann et al., 2010; Huang et al., 2008; Knopp et al., 2009; Sperling and Parak, 2010), nanotubes (W, 2010; Tasis et al., 2006; Wang et al., 2008; Zhao and Stoddart, 2009), nanowires (Suspene et al., 2010; Simpkins et al., 2007; Park et al., 2007; Skinner et al., 2006), and other nanostructures (Nicu and Leichle, 2008; Sadik et al., 2009) improves the response properties and sensing mechanisms that superior to entrapment of ionophores within the polymeric structure of ion-selective membranes. It was seen that addition of silver nanoparticles to the carbon paste matrices via increasing the tendency of the functional group of immobilized MWCNT improves the characteristic performances and figures of merit of proposed electrodes.

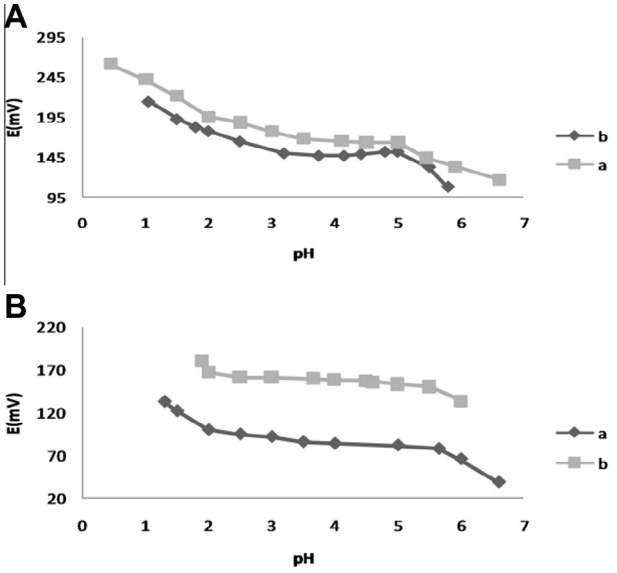

Figure 5 Effect of pH of the test solution of Cu^{2+} on the potential response of the Cu^{2+} ion-selective electrode (a): 10^{-1} M, (b): 10^{-2} M. (A): CMMWCNT, (B): CMMWCNT and Ag particles.

3.1. Effect of pH

The influence of pH on the potentiometric response of these new proposed electrodes in the pH range of 1.5 to 6.0 at 1.0×10^{-2} and 1.0×10^{-3} mol L^{-1} of Cu^{2+} ion solution was investigated and the result is shown in Fig. 5. The operational range was studied by changing the pH of the test solution with dilute HNO_3 and/or NaOH. As it can be seen, the potentials remain constant in the pH range of 2.0–5.5 as the working pH range of proposed electrodes. It seems, at higher pH via simultaneous formation of hyrdoxo complexes or hydroxide precipitate or because of probable change in stoichiometry of metal chelate species a drift in response was achieved. At low pH values by protonation of proposed carrier and various functional groups of graphite powder or activated MWCNT, the response performance significantly decreased. Since the pH of Cu^{2+} ion solution over linear range is in this range, this pH range was selected as the working range without addition of buffer.

3.2. Potentiometric selectivity

The potentiometric selectivity coefficients of these new electrodes were evaluated by the conventional method such as the separate solution method (SSM) (at 0.01 M of ions) and fixed interference method (FIM) (0.01 M interfering ions and different concentration of Cu^{2+} ion) and numerical calculated value of selectivity coefficient was calculated and presented in Table 3. As shown in Scheme 1, a tridentate (N_2O) Schiff base has been generated on the MWCNT surface. A hard donor atom (O) and two relative hard atoms (N) are suitable chelating agents for binding to hard and relatively hard cations. This surface supported Schiff base that can be deprotonated via phenolic OH and NH groups and act as two basic chelating agents. Many reports have been done on complexation of copper (II) ion with Schiff bases containing N_2, N_2O_2, N_4, N_2S etc. (Cerchiaro et al., 2005; Karabocek et al., 2007; MacDonald et al., 1982). Therefore, it is expected that the

Table 3 Selectivity coefficients of the Cu^{2+} ion carbon paste electrodes by the separate solution method (SSM) (at 0.01 M of ions) and fixed interference method (FIM) (0.01 M interfering ions and different concentrations of Cu^{2+} ion).

Ion	−LogK			
	CMMWCNT		Ag	
	FIM	SSM	FIM	SSM
Na^{+}	1.45	1.35	1.69	1.88
Zn^{2+}	3.25	2.75	2.81	2.49
Ni^{2+}	3.17	2.67	2.86	2.69
Pb^{2+}	1.18	1.21	2.42	1.36
Cd^{2+}	3.27	2.73	2.76	1.33
Fe^{3+}	1.17	0.96	1.45	1.03
K^{+}	1.41	1.62	1.54	2.63
Ca^{2+}	2.25	2.72	3.11	2.54
Co^{2+}	2.41	1.87	3.28	3.14

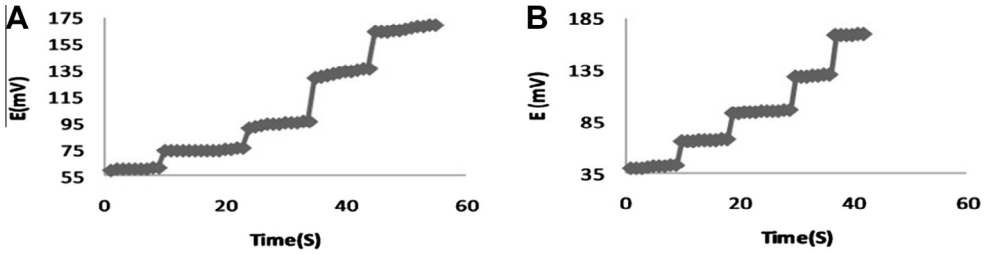

Figure 6 Response time of proposed Cu^{2+} ion selective electrode based on (A): CMMWCNT, (B): CMMWCNT and Ag particles over the different concentrations in the range of 1.0×10^{-8} to 1.0×10^{-1} mol L^{-1}.

copper ion as relative hard cation reacts with this chelating agent in 1:1 and/or 1:2 ratio. Other hard cations maybe inferred with Cu^{2+} based on the extent of their hardness as shown in Table 3.

This phenomena, efficiently show that Cu^{2+} ion interacts via a specific type of interaction and carriers' structure play a considerable role on the response of the electrodes.

3.3. Dynamic response time

It is well known that the dynamic response time of a sensor is one of the most important factors in its evaluation. This property was examined at required time to achieve equilibrium response over the different concentrations in the range of 1.0×10^{-8} to 1.0×10^{-1} mol L^{-1} and typical curve is presented in Fig. 6. The electrode based on Ag-NP-AC has fast and repeatable response mechanism at about 10 s and is stable for at least 10 min. The similar response time in opposite direction shows the reversibility and usability of proposed electrodes in different real samples with various contents of analytes. The electrode simply is applicable for Cu^{2+} ion content evaluation by simple re-newing of the electrode surface on paper to remove residual adsorbed copper content on the surface of carbon paste electrode. The standard deviation of slope of similar electrodes at optimum conditions specified above ($N = 6$) was between 1.42 and 1.65. The simultaneous re-calibration of the same electrode at optimum conditions shows no significant change in linear range with standard deviation of slope between 1.74 and 1.89. The overall characteristic performance of all proposed electrodes is presented in Table 4.

Table 4 Specification of proposed electrodes based on CMMWCNT.

Properties	Values/range	
	(CMMWCNT)	
Electrode type		Carbon paste electrode
Optimized carbon pasted composition (% by weight)	Carbon powder, CMMWCNT, Nujol, NaTPB (mg) (50: 100, 36, and 6 mg)	Carbon powder, CMMWCNT, Nujol, NaTPB, Ag (mg) (50: 100, 36, 6, and 5 mg)
pH range	2.0–5.0	2.0–5.5
Linear range (M–M)	5.0×10^{-6}–1.0×10^{-1}	5.0×10^{-7}–1.0×10^{-1}
Slope (mV/decade)	29.93	29.11
SD[a]	1.52	1.29
Response time (s)	<15	≈ 10

[a] Standard deviation of slope (within electrode variation, mV/decade).

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Table 5 Application of the proposed electrodes for the determination of copper ion in water samples.

Sample	Added	CMMWCNT		CMMWCNT-Ag	
		Found	Recovery[a]	Found	Recovery [a]
Cinnamomum zeylanicum	0	21.8 ± 0.6	–	21.5 ± 0.4	–
	50	72.4 ± 0.7	101.2	72.0 ± 0.9	101.0
ZINGIBER OFFICINALE	0	26.6 ± 0.7	–	26.2 ± 0.5	–
	50	77.2 ± 0.4	101.2	76.4 ± 0.6	100.4

3.4. Determination of Cu^{2+} ion in real samples

The proposed electrodes were applied successfully for Cu^{2+} ion content evaluation in Cinnamomum zeylanicum and Zingiber officinal that were treated according to experimental section. In these real samples, the analyte content in spike samples was evaluated by the standard addition method and respective results are presented in Table 5. As it was observed, the low RSD and high recovery of the proposed method indicate its applicability for Cu^{2+} ion determination in various real samples. The proposed electrode was also successfully applied as an indicator electrode in conjunction with Ag/AgCl reference electrode for the potentiometric solutions with Cu^{2+} ion.

4. Conclusions

A new Cu^{2+} ion selective electrode by impregnation of chemically modified MWCNT in the graphite powder was constructed that is superior to other previously reported Cu^{2+} ion selective electrode in terms of wider working concentration range and shorter response time (1.0×10^{-7} to 1.0×10^{-1} mol L^{-1}) with low response time (15 s). This sensor shows good selectivity, high sensitivity and is better than some reported Cu^{2+} selective sensors .The proposed sensor is better when compared to the reported sensors in terms of working concentration range and response time. This chemically modified carbon paste electrode (CMCPE) preparation using this new ionophore is very simple and fast undoubtedly represents one of the most convenient materials for the preparation of modified Cu^{2+} ion carbon paste electrode. As the proposed sensor shows high sensitivity wider working concentration range and good selectivity it could be used for the determination of Cu^{2+} in various samples (Cinnamomum zeylanicum and Zingiber officinale) and is therefore a good addition to the family of Cu^{2+} selective sensors.

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